

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
8 April 2004 (08.04.2004)

PCT

(10) International Publication Number
WO 2004/028673 A1

(51) International Patent Classification⁷: **B01D 69/02**,
67/00, A61K 9/00, B01D 61/42

(21) International Application Number:
PCT/EP2003/010631

(22) International Filing Date:
24 September 2003 (24.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
102 44 914.7 25 September 2002 (25.09.2002) DE
10/254,947 25 September 2002 (25.09.2002) US

(71) Applicant (for all designated States except US):
**GESELLSCHAFT FUER SCHWERIONEN-
FORSCHUNG MBH** [DE/DE]; Planckstrasse 1, 64291
Darmstadt (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SIWY, Zuzanna**
[PL/DE]; Würzburgerstr. 18, 64291 Darmstadt (DE).
BEHREND, Jan [DE/DE]; Georgenstrasse 53, 80799
München (DE). **FERTIG, Niels** [DE/DE]; Loristr. 9,
80335 München (DE). **FULINSKI, Andrzej** [PL/PL];

Aleje Slowackiego 15/6, PL- Krakau (PL). **MARTIN, Charles, R.** [US/US]; 2135 NW 28th Street, Gainesville, FL (US). **NEUMANN, Reinhard** [DE/DE]; Jahnstr. 50, 69221 Dossenheim (DE). **TRAUTMANN, Christina** [DE/DE]; Würzburgerstr. 18, 64291 Darmstadt (DE). **TOIMIL MOLARES, Eugenia** [ES/DE]; Dieburgerstr. 241/7, 64291 Darmstadt (DE).

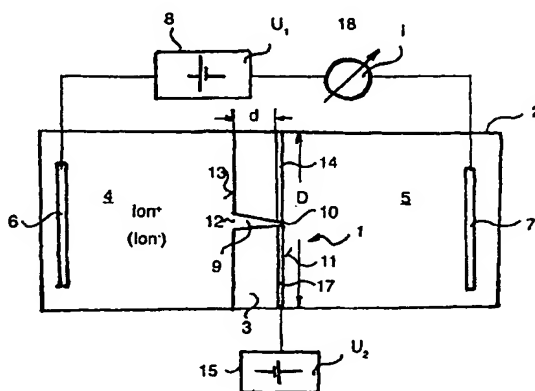
(74) Agents: **BOETERS, Hans, D.** et al.; Boeters & Lieck, Bereiteranger 15, 81541 München (DE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: NANODEVICE FOR CONTROLLED CHARGED PARTICLE FLOW AND METHOD FOR PRODUCING SAME



(57) Abstract: The present invention relates to an apparatus having a nanodevice (1) for controlling the flow of charged particles in an electrolyte. Such apparatus comprises an electrolytic bath container (2) divided by a polymeric membrane foil (3) into a first (4) and a second compartment (5), wherein each compartment (4, 5) comprises an electrode (6, 7) connected to a voltage supply (8). Further the apparatus comprises at least one asymmetric pore (9) forming a via hole through said foil (3), wherein said pore (9) provides a narrow opening (10) of a diameter in the range of several nanometers down to about one nanometer on a front side (11) of said foil (3) and a wide opening (12) in the range of several ten nanometers up to several hundred nanometers on a back side (13) of said foil (3). Further, the apparatus comprises an electrically conductive layer (14) surrounding said narrow opening (10) on said front side (11) and a gate voltage supply (15) connected to said electrically conductive layer (14) on said front side (11) of said foil (3) controlling the flow of charged particles within said nanodevice (1) from said first compartment (4) to said second compartment (5) vice versa. The invention further relates to a method for producing such a nanodevice (1).

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Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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NANO DEVICE FOR CONTROLLED CHARGED PARTICLE FLOW AND METHOD FOR PRODUCING SAME

Description

The present invention relates to a apparatus having a nano-device for controlling the flow of charged particles in electrolytes and method for producing same.

In many electrolytic systems the problem of controlling ion flow, rather than flow of electrons, is crucial. For the flow of electrons diodes and transistors are the basic elements controlling, switching on and off and amplifying the signal. For the ionic current there exist very limited possibilities to tune the ion flow. From German patent application 100 44 565.9 an electrochemical rectifier is known, based on preparation of asymmetric pores in a polymeric foil. One mode of operation entails applying a constant voltage across a membrane with asymmetric pores, however changing the current would require changing the concentration and/or the pH-value of the electrolyte. Since this changing of concentration and/or pH-value is time consuming and disturbs the condition

of operation, this option may not be applicable for a given system.

Therefore, it is the object of the present invention to provide an independent "switch", which would be able to modulate the ion current through the pore with a minimum disturbance of the operation conditions. Further, it is an object of the present invention to control the transport of charged or ionized large molecules.

According to the invention an apparatus having a nanodevice for controlling the flow of charged particles in electrolytes is provided, comprising an electrolytic bath container, divided by a polymeric foil into a first and a second compartment. Each compartment comprises an electrode connected to a voltage supply. Further, the nanodevice comprises at least one preferentially asymmetric pore forming a via hole through said foil, wherein said pore provides a narrow opening of a diameter in the range of several nanometers down to about one nanometer on a front side of said foil and a wide opening in the range of several ten nanometers up to several hundred nanometers on a back side of said foil.

The polymeric foil is covered on its front side by an electrically conductive layer surrounding said narrow opening. A gate voltage supply is connected to said electrically conductive layer on said front side of said foil controlling the flow of charged particle within said nanodevice from said first compartment to said second compartment and vice versa.

This nanodevice has the advantage to control or to switch on and off a charged particle flow of heavy ions, ions of macromolecules, ions of bio-molecules, ionized dimeric,

ionized oligomeric or ionized polymeric DNA or ionized insulin. In such a nanodevice with such a pore the spatial distribution of electric potential inside the pore is changed by the gate voltage on the electrically conductive layer of the polymeric foil in order to advantageously tune the flow of ion through the pore. The electrically conductive layer forms a gate close to the narrow opening of the conical, funnel-like, or trumpet-like pore or at the entrance of a cylindrical pore, where the pore has its highest resistance. Such a gating ion flow would allow to control ionic current through the asymmetric pore.

In a preferred embodiment the polymeric foil comprises polyethylene terephthalate, polyimide or polycarbonate. These materials have the advantage, that an ion trace can be performed through said foil by a high accelerated ion like bismuth. Such a trace across a foil material can be etched in an electrolytic cell consisting of two cell halves filled with an electrolytic solution and being divided by said foil comprising said ion trace. These materials have further the advantage that a nanodevice made of same is cation selective.

Another preferred embodiment comprises a gold layer as electrically conductive layer surrounding said narrow opening of said front side. Such a gold layer as a gate electrode has the advantage, that it is resistive against corrosion and oxidation. Therefore, such gold layer can be used in different electrolytic bathes to control and/or switch on an off a flow of charged particles.

Another preferred material for the gate electrode is a semiconductor like indium oxide or ITO. Indium oxide has the

advantage, that it is erosion and oxidation resistant in almost any electrolytic bath.

In a further preferred embodiment the back side of said foil is covered by an electrically conductive layer surrounding said wide opening. Such a second metal layer on the back side of the polymeric foil enables the nanodevice to make the ion current changes finer and better controlled.

The nanodevice is not limited either to polymer films or to a gold layer, since any asymmetric and charged nanopores together with a conductive layer, which can be charged by a voltage, can be potentially used to accomplish the present invention.

A membrane with asymmetric pores enables an optimal control of the particle flow, offering at the same time higher mass flow than a corresponding cylindrical pore of the same effective diameter. The principles of functioning of the nanodevice are valid however also for symmetric, for example, cylindrical pores with a metal (or semiconductor) layer sputtered on one side of the membrane. This broadens immensely the possibilities of manufacturing a device of this kind, because also commercially available membranes with cylindrical pores of any material (e.g. polymer, anodic alumina) can be used. By applying voltage to the layer, it makes the system asymmetric as far as distribution of electric potential inside the pore is concerned.

Covering the conductive layer by a thin insulating layer that is chemically inactive in an electrolyte solution limits the influence of the "gate" potential to the entrance of the pore

with said layer. This is expected to improve the control over the charged particle flow.

Ion flow control is possible also with pores of diameter up to hundreds of nm. In said large-pore set-up the layer representing the third electrode is preferentially made of a non-insulating i.e. electrically conductive material. The pores are not selective with respect to different ion species, and the mechanism of ion flow control differs from that in very narrow pores. The potential on the conductive layer (U_2) superimposes the potential difference applied across the membrane (U_1), which for given voltage configurations provides the possibility of enhancing or stopping anions (cations). This was demonstrated with a membrane containing 10^7 pores/cm² and methylene blue dye.

One preferred mode of operation of the nanodevice is to provide a direct current voltage supply for the electrolytic bath and a direct current voltage supply for the gate voltage. Another preferred mode of operation is to apply an alternating voltage to the gate, which enables to achieve a pulse-like flow of charged molecules through said nanodivice with at least one asymmetric pore.

Preferred applications of the apparatus having a nanodevice are

1. Separation processes for the pharmaceutical industry,
2. Controlled release of bio-molecules like insulin,
3. Voltage-controlled nanosystems,
4. Tuning of the ion current signal,
5. Gating of ionic bio-molecule in microfluidic lab-on-a-chip devices.

The invention is further related to a method for producing a nanodevice. Such a method comprises the steps of:

- irradiating a membrane of a polymeric foil by at least one high accelerated ion to form an ion trace through said foil;
- etching said ion trace from a back side of said foil toward a front side of said foil to form a pore having a wide opening on said back side in the range several ten nanometers up to several hundred nanometers and a narrow opening on said front side in the range of several nanometers down to about one nanometer;
- drying said etched foil;
- depositing an electrically conductive layer on said front side by diminishing the narrow opening;
- reopen said narrow opening to a predetermined diameter by etching said conductive layer from its back side.

This method has the advantage that a conical, a funnel-like or a trumpet-like nanopore is performed along the ion trace through the polymeric foil dependent on the parameters of an electrolytic process in an electrolytic cell consisting of two cell halves filled with an electrolytic solution.

In a preferred method at least a single bismuth ion is accelerated to an energy in the range of 10 to 15 MeV and irradiated toward said polymeric foil to form said ion trace. This bismuth ion is particularly advantageous if applied to foils made of polyethylene terephthalate, polyimide and/or polycarbonate. This trace is preferably etched by a caustic solution, where such a solution can comprise 9m NaOH. This caustic solution has the advantage that the ion trace can be etched at room temperature. After etching along the ion trace an asymmetric pore, the front side of the foil is deposited

with a electrically conductive layer like a gold or indium oxide layer by a sputter technique.

To increase the adhesiveness of an electrically conductive layer like a gold layer or a semiconductor layer on the polymer surface of the foil, it is an advantage to roughened the surface of the polymer foil before etching the irradiated film.

During said deposition of a metal or a semiconductor on said front side the narrow opening is diminished. To reopen said narrow opening a piece of a conductive tape is attached to cover the conductive layer. After that it is an advantage to reinsert said foil with its electrically conductive layer and said piece of a conductive tape in an electrolytic cell, wherein the two cell halves are filled with potassium fluoride, whilst a conductive tape stays attached to the conductive layer.

Further embodiments, features and advantages of the invention are now discussed with reference to the attached drawings.

Fig. 1 shows a schematic drawing of an apparatus having a nanodevice for controlling the flow of charged particles in electrolytes.

Fig. 2 shows principles of the functioning of the nanodevice for controlling the flow of charged particles in electrolytes.

Fig. 3 shows a scheme of an experimental set-up for evaluating the performance of the nanodevice.

Fig. 4 shows current-voltage characteristics of a single conical pore in a polyethylene terephthalate (PET) foil with a gold layer on the side of the small or narrow opening of a pore, applying 0.1m KF on both sides of the membrane foil.

Fig. 5a,b show examples of time series without and with applied "gate voltage" for two directions of the potassium ion flow.

Figure 1 shows an embodiment of an apparatus having a nanodevice 1 for controlling the flow of charged particles (ion^+ or ion^-) in an electrolyte. This device comprises an electrolytic bath container 2 divided by a polymeric foil 3 into a first 4 and a second 5 compartment. Each compartment 4 and 5 comprises an electrode 6 and 7 connected to a voltage supply 8, which supplies in this embodiment a direct current voltage U_1 . The electrolytic current I is measured by a current meter 18.

If the potential of electrode 6 is positive, positive charged particles like ion^+ are forced through the asymmetric pore 9 of the foil 3 from a wide opening 12 on the back side 13 of the foil 3 to a narrow or small opening 10 on the front side of said foil 3. The foil itself is a circular disc having a diameter D of about 30 mm and a thickness d of 12 μm . The material of the foil in this embodiment is polyethylene terephthalate which was irradiated in its center with a single bismuth ion of 11.4 MeV specific energy and etched from one side in a 9m NaOH at room temperature to form said pore 9.

The polymeric foil 3 is covered on the front side 11 by a gold layer surrounding the narrow opening 10 of said pore 9. This

gold layer functions as a gate electrode 17, which is supplied by a gate voltage U_2 supply 15. If this gate voltage U_2 is negative, the charged particles in the first compartment 4 like ion^+ are accelerated, so that the flow through the nanodivice 1 is increased toward the second compartment 5. When Increasing U_2 toward a positive gate voltage the flow of positive charged particles (ion^+) is decreased and can even be switched off.

Figure 2 shows principles of the functioning of the nanodevice 1 for controlling the flow of charged particles (ion^+ , ion^-) in electrolytes. Components with the same functions as in Figure 1 are characterized by the same reference signs and an explanation of same is omitted.

Figure 2 shows in detail the principles of operating a device shown in Figure 1. A thin layer 14 of metal or semiconductor is sputtered on the front side 11 of the foil 3 having such narrow openings 10. This layer 14 can be charged via an independent electric circuit U_2 . If the pore is very narrow, the passage of the ions through the pore will be influenced by such a "gate". The pore produced by a track-etching technique in a foil 3 made of polyethylene terephthalate, polyimide or polycarbonate are negatively charged due to formation of carboxylate groups, therefore they are cation-selective. This means that cations are the main charge carriers.

Applying a positive voltage U_2 slows down the flow of cations observed as lower current. Applying a negative voltage U_2 has an opposite effect, the current will be larger. Accordingly, this device will be the first device, which can control the ion flow, based on asymmetry of electric potential introduced by the conical, funnel-like or trumpet-like shape of a charged

nanopore in combination with applying locally electric fields. Since this layer can be charged positively or negatively by means of the voltage applied via an independent circuit, this results in changes of the profile of the electric potential at the pore constriction, which influences the ion current flow.

Figure 3 shows a scheme of an experimental set-up of evaluating the performance of the nanodevice 1. Components having the same functions as in Figure 1 or in Figure 2 are characterized by the same reference signs and an explanation of same is omitted.

The evaluation of the performance of the nanodevice 1 is made for a single pore within a 12 μm thick circular disc of 30 mm diameter. For the purpose of etching such a pore in a 9m NaOH this disc or membrane is inserted between two halves of an electrolytic cell and sealed hermetically by applying pressure onto the two cell halves. When the etching process is completed, the polymer foil 3 is removed from the cell and dried. In a next step, a gold layer 14 is sputtered on the front side 11 with its narrow opening 10. Then, a piece of a conductive tape is attached to the front side onto the gold layer. Now, the foil is inserted back into the electrolytic cell, which chambers are now filled with potassium fluoride.

The current through the pore 9 is measured with electrodes of Ag/AgCl. An independent circuit is built, which applies a voltage to the gold layer via the conductive tape. The scheme of the experimental set-up is shown in Figure 3. The use of fluoride ions in a KF solution increases the effect of the applied voltage during the electrolytic procedure. F^- ions do not adsorb to the gold layer.

Figure 4 shows a current-voltage characteristic of a single conical pore 9 in a PET-foil. The abscissa of said diagram shows the voltage U_1 in V and the ordinate shows the current in nA. The dotted curves shows the effect of the parameters: +0.6 V at the metal gate electrode, 0V at the metal gate and -0.6 V at the metal gate. As one can see from this evaluation it is possible to enhance the current through the asymmetric pore at a voltage U_1 of 0.4 V by a gate voltage U_2 of -0.6 V up to around 1 nA, whilst with a positive gate voltage of 0.6 V the ionic current is decreased to 0 or shut off.

Figures 5a and 5b show examples of time series without and with applying a gate voltage for two directions of the potassium ion flow. If a voltage of +2V is applied across the membrane a voltage of +1.5V at the gate will decrease the current drastically, whilst a gate voltage of -1.5 will increase the current up to 1nA. In these diagrams of Figures 5a and 5b the abscissa shows the time in seconds and one can see that after three seconds the current is relatively constant.

In Figure 5b the voltage across the membrane or across the pore is changed to -2V, so that the current is also negative. By applying negative gate voltage of about -1.5V the current is decreased, whilst applying a positive gate voltage of 1.5V the current is increased to -1nA. This diagrams show that this nanodevice is quite sensitive and works like a triode for ions in an electrolytic bath.

List of reference signs

- 1 nanodevice
- 2 electrolytic bath container
- 3 polymeric foil
- 4 first compartment
- 5 second compartment
- 6 electrode
- 7 electrode
- 8 voltage (U_1) supply
- 9 asymmetric pore
- 10 narrow opening
- 11 front side
- 12 wide opening
- 13 back side
- 14 electrically conductive layer
- 15 gate voltage (U_2) supply
- 16 electrode
- 17 gate electrode
- 18 current meter

Claims

1. An apparatus having a nanodevice for charged particles flow comprising
 - an electrolytic bath container (2), divided by a polymeric foil (3) into a first (4) and a second (5) compartment, wherein each compartment (4, 5) comprises an electrode (6, 7) connected to a direct current voltage (U_1) supply (8);
 - at least one preferentially asymmetric pore (9) forming a via hole through said foil (3), wherein said pore (9) provides
 - a narrow opening (10) of a diameter in the range of several nanometers down to about one nanometer on a front side (11) of said foil (3) and
 - a wide opening (12) in the range of several ten nanometers up to several hundred nanometers on a back side (13) of said foil (3);
 - an electrically conductive layer (14) surrounding said narrow opening (10) on said front side (11);
 - a gate voltage (U_2) supply (15) connected to said electrically conductive layer (14) on said front side (11) of said foil (3) controlling the flow of charged particles within said nanodevice (1) from said first compartment (4) to said second compartment (5) and vice versa.
2. The apparatus according to claim 1, **characterized in that** said preferentially asymmetric pore (9) is a preferentially conical pore.
3. The apparatus according to claim 1, **characterized in that** said preferentially asymmetric pore (9) is a funnel-like

pore from said wide opening (12) toward said narrow opening (10).

4. The apparatus according to claim 1 or claim ,
characterized in that said asymmetric pore (9) is a straight trumpet-like pore from said narrow opening (10) toward said wide opening (12).
5. The apparatus according to any one of claims 1 to 4,
characterized in that said foil (3) comprises polyethylene terephthalate.
6. The apparatus according to any one of claims 1 to 4,
characterized in that said foil (3) comprises any polymer, preferentially polyimide.
7. The apparatus according to claim 1, **characterized in that** said foil (3) comprises polycarbonate.
8. The apparatus according to any one of claims 1 to 7,
characterized in that said nanodevice (1) is ion selective.
9. The apparatus according to any one of claims 1 to 8,
characterized in that said electrically conductive layer (14) surrounding said narrow opening (10) on said front side (11) comprises gold.
10. The apparatus according to any one of claims 1 to 8,
characterized in that said electrically conductive layer (14) surrounding said narrow opening (10) on said front side (11) comprises indium oxide.

11. The apparatus according to any one of claims 1 to 10,
characterized in that said electrically conductive layer (14) surrounding said narrow opening (10) on said front side (11) is a gate electrode (17).
12. The apparatus according to any one of claims 1 to 11,
characterized in that said back side (13) of said foil (3) is covered by an electrically conductive layer (14) surrounding said wide opening (12).
13. The apparatus according to any one of claims 1 to 12,
characterized in that said nanodevice (1) is applied to control or to switch on and off a charged particle flow of heavy ions, ions of macromolecules, ions of biomolecules, ionized dimeric, ionized oligomeric or ionized polymeric DNA or ionized insulin.
14. A method for producing a nanodevice (1) of an apparatus according to one of the claims 1 to 13 comprising the steps of:
 - irradiating a membrane of a polymeric foil (3) by at least one highly accelerated ion to form an ion trace through said foil;
 - etching said ion trace;
 - drying said etched foil (3);
 - depositing an electrically conductive layer (14) on said front side (11) by diminishing the narrow opening (10);
 - reopen said narrow opening (10) to a predetermined diameter by etching said conductive layer (14) from its back side (13).

15. The method according to claim 14, wherein a single bismuth ion is accelerated to an energy in the range of 10 to 15 MeV and irradiated toward said polymeric foil (3) to form said ion trace.
16. The method according to claim 14 ore claim 15, wherein said ion trace is etched by a caustic solution.
17. The method according to claim 16, wherein said caustic solution comprises 9m NaOH.
18. The method according to one of the claims 14 to 17, wherein said ion trace is etched at room temperature.
19. The method according to one of the claims 14 to 18, wherein said deposition is carried out by sputtering a metal or a semiconductor on to said front side (11).
20. The method according to one of the claims 14 to 19, wherein said front side (11) of said foil (3) is roughened before etching said ion trace.
21. The method according to one of the claims 14 to 20, wherein said membrane is inserted in an electrolytic cell consisting of two cell halves filled with a KF solution and being divided by said membrane and sealed hermetically to etch said ion trace.
22. The method according to one of the claims 14 to 21, wherein a conductive tape is attached to the conductive layer (14) before said reopening of said narrow opening (10) is performed.

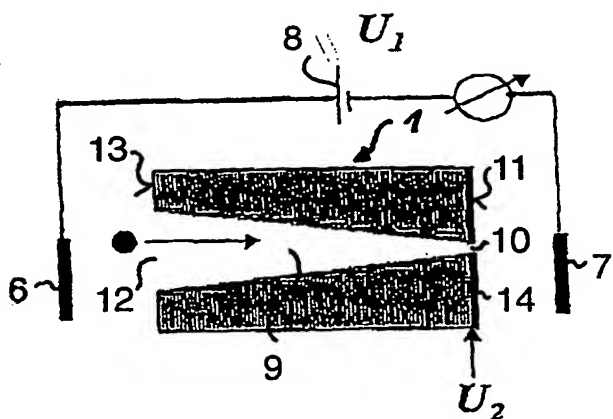
23. The method according to claim 22, wherein said foil covered on its front side (11) by a conductive tape is reentered to said electrolytic cell, which cell halves are now filled with NaF.
24. A method to control an ion flow with pores of a diameter up to hundreds of nm within a membrane, wherein said large-pore set-up the layer to represent the third electrode of an electrically conductive material, wherein the pores are not selective with respect to different ion species and wherein the potential on the conductive layer (U_2) superimposes the potential difference applied across the membrane (U_1), which for a given voltage configuration provides an enhancing or a stopping of ions.
25. The method of claim 24, wherein the membrane contains 10^7 pores/cm² and is made of a methylene blue dye.

U



Fig. 2

2/3



- 1) $U_2 = 0$ I
 2) $U_2 > 0$ $I - \Delta I$
 3) $U_2 < 0$ $I + \Delta I$

Fig. 3

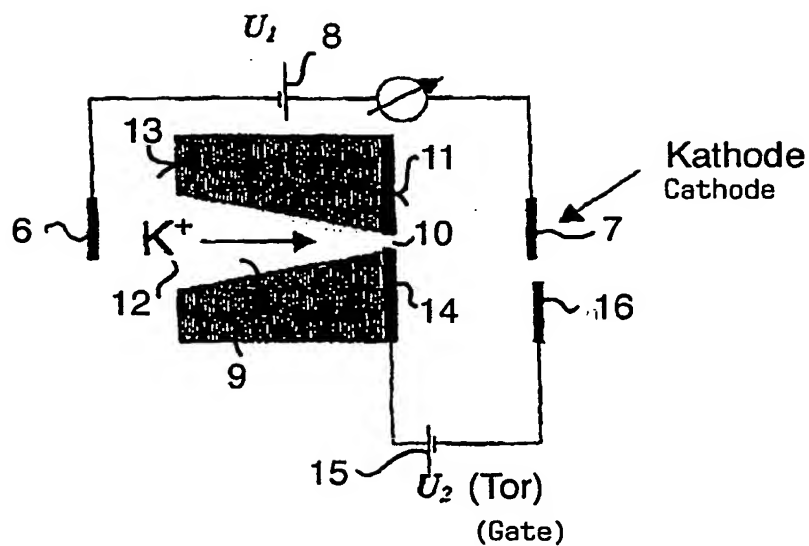


Fig. 4

3/3

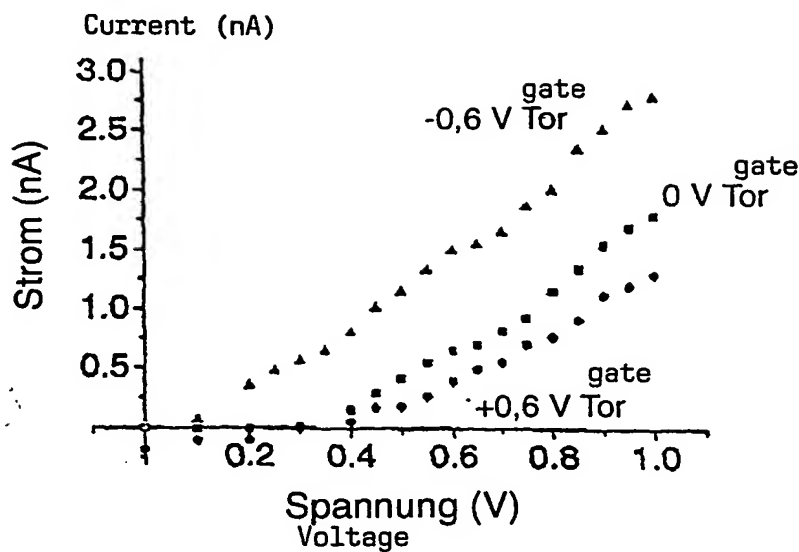


Fig. 5a

+2 V an die Membran angelegt

+2 V applied across the membrane

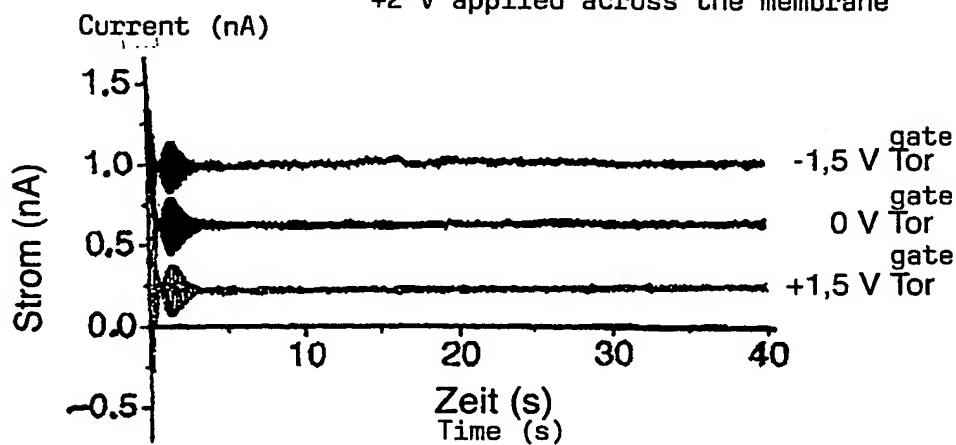
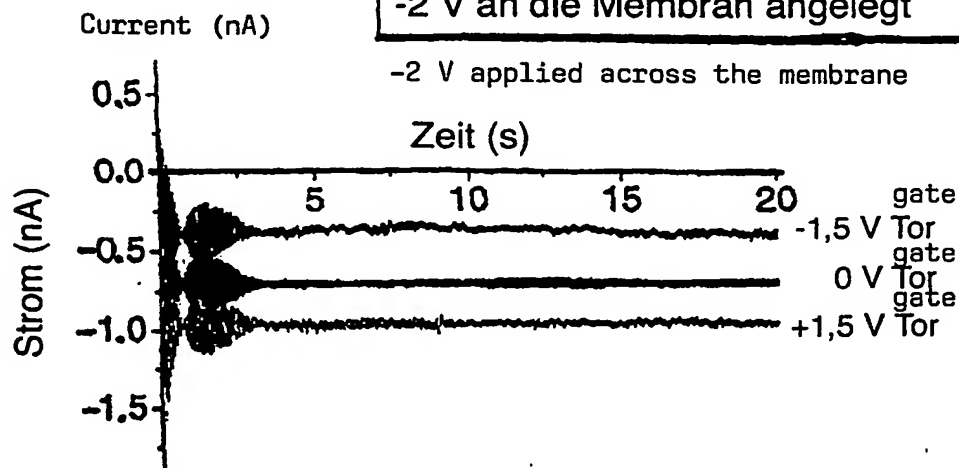


Fig. 5b

-2 V an die Membran angelegt

-2 V applied across the membrane



INTERNATIONAL SEARCH REPORT

International Application No.

03/10631

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D69/02 B01D67/00 A61K9/00 B01D61/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EP0-Internal, COMPENDEX, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 02 20877 A (SPOHR REIMAR ; SCHWERIONENFORSCH GMBH (DE); KORCHEV YURI (GB); YOSH) 14 March 2002 (2002-03-14) figure 5 --- -/--	1-13, 24, 25

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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International Application No.

03/10631

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 012, no. 037 (C-473), 4 February 1988 (1988-02-04) -& JP 62 186904 A (KIYOSHI SUGAI), 15 August 1987 (1987-08-15) abstract; figures 1,3-5,8,10 -& DATABASE WPI Section Ch, Week 198738 Derwent Publications Ltd., London, GB; Class J01, AN 1987-268003 XP002226679 & JP 62 186904 A (SUKAI K), 4 February 1988 (1988-02-04) abstract	1-13,24, 25
A	--- US 5 736 050 A (PASTERNAK CHARLES A ET AL) 7 April 1998 (1998-04-07) column 3, line 18 -column 4, line 44; claims 1,3,5,8; figure 2; examples 1,2	1,5,24
A	--- US 5 593 560 A (INOUE NOBORU) 14 January 1997 (1997-01-14) column 9, line 26 -column 10, line 40; figure 1	1-3,24
A	--- DE 198 53 286 A (SCHWERIONENFORSCH GMBH) 25 May 2000 (2000-05-25) figure 1	1,24
A	--- PATENT ABSTRACTS OF JAPAN vol. 002, no. 126 (C-025), 21 October 1978 (1978-10-21) & JP 53 091079 A (TOKUYAMA SODA CO LTD), 10 August 1978 (1978-08-10) abstract -& DATABASE WPI Section Ch, Week 197837 Derwent Publications Ltd., London, GB; Class J01, AN 1978-66151A XP002269273 & JP 53 091079 A (TOKUYAMA SODA KK) abstract	1,24
A	--- WO 02 36230 A (HAMMERSTEDT ROY H ;LAREDO WALTER (US); ALLCOCK HARRY R (US); BENDE) 10 May 2002 (2002-05-10) page 3, line 24 -page 4, line 3; claims 1,7 -----	1,14,24

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP 03/10631

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0220877	A	14-03-2002	DE 10044565 A1 WO 0220877 A1 EP 1315851 A1	04-04-2002 14-03-2002 04-06-2003
JP 62186904	A	15-08-1987	NONE	
US 5736050	A	07-04-1998	AU 5821094 A DE 69409223 D1 DE 69409223 T2 EP 0678051 A1 WO 9415701 A1 JP 8505318 T	15-08-1994 30-04-1998 16-07-1998 25-10-1995 21-07-1994 11-06-1996
US 5593560	A	14-01-1997	DE 4308390 A1 JP 2109828 C JP 5345147 A JP 8000210 B	23-09-1993 21-11-1996 27-12-1993 10-01-1996
DE 19853286	A	25-05-2000	DE 19853286 A1 AT 228351 T DE 59903606 D1 DK 1148869 T3 WO 0030606 A1 EP 1148869 A1	25-05-2000 15-12-2002 09-01-2003 10-03-2003 02-06-2000 31-10-2001
JP 53091079	A	10-08-1978	JP 1450194 C JP 62060125 B	11-07-1988 15-12-1987
WO 0236230	A	10-05-2002	AU 3395802 A EP 1345760 A2 US 2002088748 A1 WO 0236230 A2	15-05-2002 24-09-2003 11-07-2002 10-05-2002

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